

1922  
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**A STUDY OF THE FACTORS AFFECT-  
ING THE ELECTRODE POTENTIAL  
OF ZINC**

BY

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**THESIS**

FOR THE

**DEGREE OF BACHELOR OF SCIENCE**

IN

**CHEMICAL ENGINEERING**

---

**COLLEGE OF LIBERAL ARTS AND SCIENCES**

**UNIVERSITY OF ILLINOIS**

1922



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UNIVERSITY OF ILLINOIS

June 1, 1922

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Arthur Rowan Murphy

ENTITLED A Study of the Factors Affecting the Electrode

Potential of Zinc.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemical Engineering.

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#### ACKNOWLEDGMENT

The author wishes to take this opportunity in expressing his sincere appreciation and thanks to Doctor Gerrit G. Dietrichson, under whose direction this investigation was carried out, and for whose co-operation and assistance he is indebted.



### Introduction

Many methods have been tried in an effort to determine the electrode potentials of the more simple metals such as zinc, silver, copper, and cadmium.

While most of the investigations carried out up to this time have been successful in the determination of the potentials of the metals in contact with concentrated solutions of their ions, it has been nearly impossible to find a method which will give results in the more dilute solutions.

The fundamental importance of electrode potentials in explaining electro-chemical reactions led to the experimentation and results which are given in this article.

Due to the limited amount of time and the many difficulties encountered, the electrode potential of zinc was the only one considered in this work.



### Theoretical

The electrode potential represents the work done in carrying unit quantity of electricity between electrode and electrolyte. The normal electrode potential has been defined as the electromotive force of a reversible electrode of the pure element against a solution in which the ion of the element is (hypothetical) molal. The electrode potential of a metal in contact with a solution containing ions of that metal, is dependent on the concentration of the ions in solution. If the ion is positive, the potential difference becomes more positive with increase in concentration. If the ion is negative, then the potential becomes more negative or less positive with increase in concentration. By saying the potential becomes more positive or more negative is meant that they are positive or negative in relation to the hydrogen electrode which is considered as zero, when the electrode values are given in reference to the hydrogen scale. All values given in this article are considered with reference to hydrogen as zero, as above stated.



### Historical

Many investigators have worked with zinc potentials, but most of these have determined the potential of the metal in contact with a saturated solution of the zinc salt, or in highly concentrated solutions. The determinations of the potential in dilute solutions seems to have given rather indefinite and varied results. In spite of this some very interesting work has been done along this line, and altho no positive solution has been derived at, the investigators have thrown light on the problem and have indicated the way to further investigation.

A brief review of the work already published on this topic will be given. It may be said at this time that the results given in this article were more or less obtained by a method of experimentation obtained by a collaboration of the conclusions of former investigators and supplemented only by original ideas which would furnish a more speedy method of determination, requiring only a limited amount of skill and in this way sacrificing the minute accuracy of the former investigators.

One of the first investigations was that of Richards and Lewis(1). They studied electrodes of zinc amalgams of different concentrations and solid zinc electrodes opposite to zinc amalgams. Measurements were made at such temperatures that the amalgams were wholly liquid, for their partial solidification is an insidious cause of error capable of producing serious results.

It was noticed by Meyer that the e.m.f. of a cell of this kind increases rapidly on standing. Altho no explanation can be given of this phenomena, one may prevent by using as an electrolyte a solution which has remained standing in contact with the amalgam for several weeks before being used. The constancy thus reached assures much greater accuracy.



very thin could otherwise be obtained. Theoretically the value of the anion or the electrolyte or the concentration of the cation should have without effect upon the results of the values obtained for cells of the type used in this investigation. This prediction was verified by experiment. The cells with electrodes of zinc amalgam were less consistent than those with calcium. A tabulation of these results is given below.

Zinc Amalgams.

	C1	C2	$\frac{C1}{C2}$	t.	E. obs.	E. calc.	$\frac{E}{T}$
1.	1	<u>1</u> 9	9	30	.02890	.02860	.0000954
2.	<u>1</u> 3	<u>1</u> 27	9	50	.02920	.02860	.0000964
3.	<u>1</u> 3	<u>1</u> 9	3	30	.01425	.01450	.0000470
4.	<u>1</u> 9	<u>1</u> 27	3	70	.01515	.01450	.0000500

The measurement of the contact potential of solid electrodes has always been subject to considerable uncertainty, due to the accident of crystallization, condition of surface polarization, and other unknown causes. It is only possible that by sufficiently increasing the extent and diversity of the surface an electrode might be obtained whose surface and potential would be the mean of a large number of different values and therefore constant. An electrode of this type consisting of a quantity of the finely divided metal perhaps a cm. in depth, packed loosely around a scale in platinum wire is most likely to satisfy the desired conditions, and experiments were made with electrodes of this sort and yielded remarkably satisfactory results. The difference in potential between the solid metal and the amalgam should be emphasized.



It is often stated that the potential of the amalgam may be considered the potential of the true metal. In the case of zinc this is true "within a few thousandths of a millivolt. The results obtained by these men are given here and really show a remarkable agreement between the potential of the zinc amalgam and that of the zinc in the solid form.

Zinc versus amalgam.

cell	t	E obs.	E calc.
1	30.0	.01175	.01160
2	0.0	.00570	.00560
3	30.0	.01170	.01160
4	36.2	.01285	.01280
5	34.5	.01270	.01260
6	32.6	.01230	.01215
7	30.0	.01170	.01160
8	28.0	.01125	.01120
9	26.6	.01095	.01080
10	26.7	.01100	.01089
11	23.2	.01045	.01030
13	15.7	.00885	.00870
14	16.0	.00890	.00875

Frank J. Mellencamp (2) in working on the application of the Gibbs-Helmholtz to concentration cells used zinc amalgams in contact with zinc sulphate solutions, and arrived at some very interesting results. As with the fault of many former investigators, his work with more or less concentrated solutions, the most dilute electrolyte used being one mol of zinc sulphate with four hundred moles of water which is approximately .14N.

He found that amalgam electrodes are best adapted for work on elec-



trode potentials of zinc. Since with the pure metal it is very difficult to prevent oxidation or to exclude occluded gases, variable and unsatisfactory results must follow. To obtain consistent results the electrode must remain reasonably constant for days. Amalgams best fulfill these conditions. The amalgams must not change phase in the temperature interval employed, that is, they must remain either solid or liquid throughout the test. The dilute an amalgam the more readily it oxidizes.

In general it took a few hours before the readings of the cells became constant. There was no regularity in the shifting of the preliminary readings; some cells assumed a high initial value and gradually fell to consistency, others started with a low initial value and rose, while still others remained constant from the very first.

Upon diluting the zinc chloride solutions, which were at first tried hydrolysis took place causing a change in concentration. The addition of the amalgam electrodes sometimes brings about this change; even a change in temperature may produce it. Taking these facts into account it is difficult to prepare a solution of zinc chloride of known concentration and to maintain it throughout the test.

Even after taking these precautions, he came to the conclusion that zinc sulphate solutions gave more persistent results than those of zinc chloride.

The first work done on the determination of the potential of zinc in dilute solutions was that of W. Grenville Horsch. He found that finely divided zinc worked satisfactorily in solutions as dilute as 0.0003 N. Therefore while there was no doubt as to the ability of zinc amalgams to give reproducible results, a study of its apparently anomalous behavior was given up, and the pure (spongy) zinc used directly.

As a matter of future reference the method employed by him in pre-



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uring his zinc chloride solution will be given here.

The zinc chloride solutions were prepared by diluting a stock solution of zinc chloride. This stock solution was prepared as follows: Pure hydrogen chloride was prepared by dropping pure concentrated sulphuric acid slowly into pure concentrated hydrochloric acid. The gas was absorbed in conductivity water until the concentration was about 0.5 N. An excess of spongy zinc, carefully washed, was then added to this acid solution and the mixture warmed gently until no further zinc would dissolve. This solution remained litmus slowly. The solution was then filtered to remove the excess zinc and the filtrate diluted to about 0.15 N and employed as a stock solution.

As has already been stated finely divided zinc was used instead of zinc amalgam because the amalgam gave unsatisfactory values of electromotive force. Between two samples of the amalgam the electromotive force varied in an erratic manner rising and falling rapidly. The finely divided zinc gave a steady value, but left something to be desired in reproducibility in the dilute solutions. For this reason the measurements were not carried out in zinc chloride solutions more dilute than 0.0003 N, and in concentrations below 0.001 N the deviation from the mean is 0.002 volts.

In the table given below are represented the observed e.m.f.'s of the cell  $\text{In} : \text{InCl} (\text{c}) ; \text{AgCl} \text{ Ag}$ .

In the second table the results given by H. Jahn are given to supplement those given in table 2. Jahn used an amalgamated zinc rod instead of pure zinc. Since as pointed out by Richards and Lewis (1), the difference in potential between pure zinc and its saturated amalgam is slight (only a few millivolts) the comparison is a fair one to make.

We found that the normal electrode potential of zinc was 0.753.



Table 1.

c. $\text{ZnCl}_2$ moles per 1000 g. water.	E (in millivolts)
0.01021	1.1550
0.001022	1.1742
0.005112	1.1955
0.001457	1.2219
0.001253	1.2380
0.000772	1.2475
0.000649	1.2497
0.0005995	1.2699
0.0003470	1.2701

Table 2.

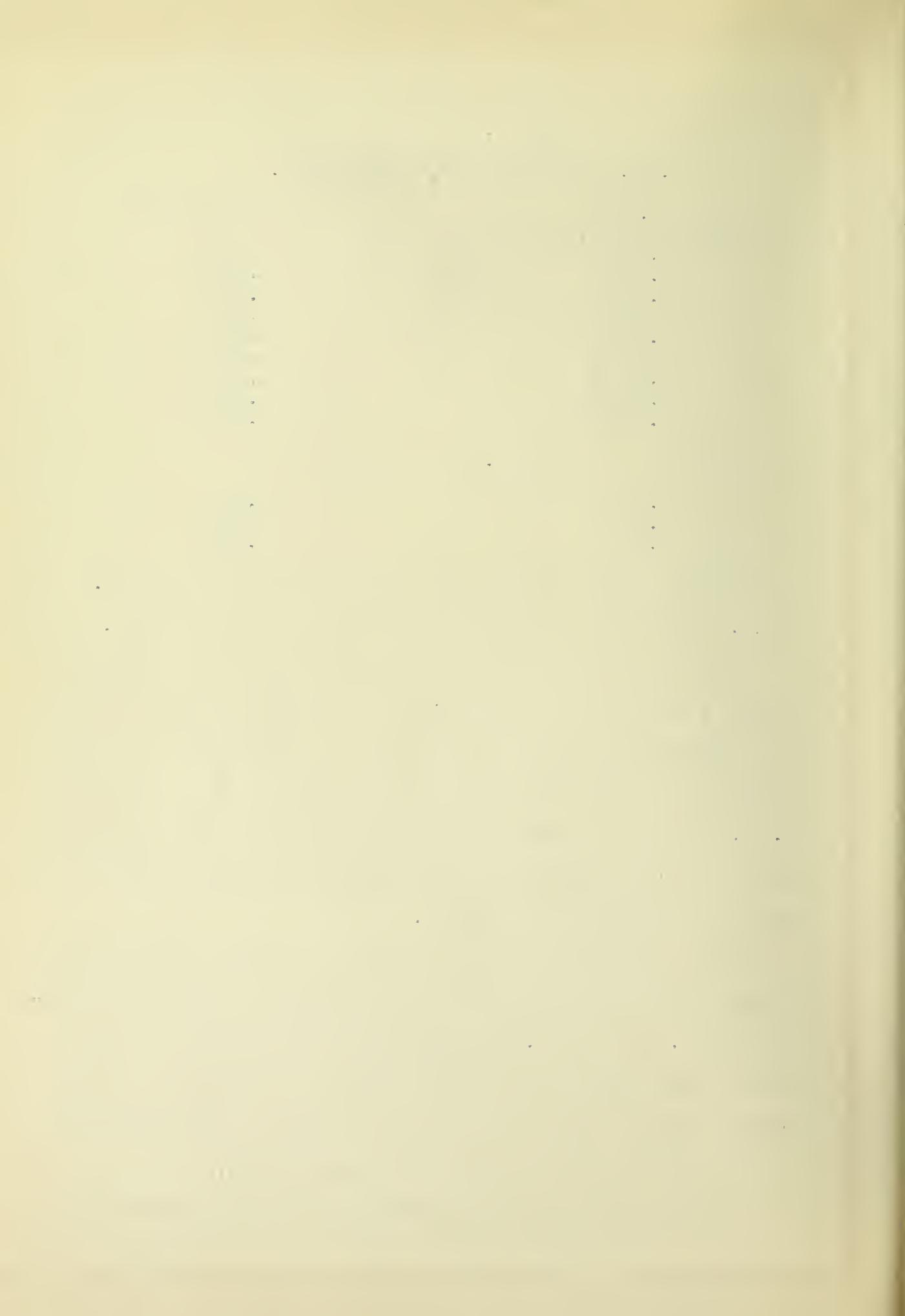
0.566	1.0306
1.112	1.0171
2.220	0.9740

The next work done on the zinc electrode was that by William C. Moore. His work was entirely confined to the use of zinc amalgams.

In a study of the literature he found that all previous investigators had confined their attention either to dilute zinc amalgams of varying composition and constant concentration of electrolyte, or to zinc amalgams or to amalgamated zinc, with salt concentrations not less than 0.5 N. Moreover in particularly all instances it was found necessary to take some sort of precaution to prevent access of atmospheric oxygen to the electrolyte and to the electrode.

Moore found in his work which dealt with the electrode potential of amalgamated zinc rods in a solution of zinc sulphate varying in concentration from 0.5 N down to 0.002 N, after considerable experimentation, that zinc electrodes reproducible at room temperature to within one millivolt could be secured by using well amalgamated zinc rods, and by bubbling hydrogen thru the zinc half-cell during the measurements.

As stated by him, Hollenbeck has shown that with an amalgam contain-



ing about 1% zinc, the temperature coefficient of the electrode potential of zinc is very small and his own work shows that changes of several degrees in the temperature have only a slight effect.

The results obtained by him are tabulated below.

Zn electrode / cat. HCl / calomel.

Con. N.	mean obs. E.	E calc.	$\alpha$
0.5	-0.784	-0.780	70
0.1	-0.800	-0.800	45
0.01	-0.823	-0.824	70
0.002	-0.840	-0.850	85

As the results of his work he arrived at the following conclusions and summary.

*experiments*

1. Observations of previous are confirmed in that it is necessary to exclude oxygen as completely as possible in setting up zinc electrodes.
2. Electrodes reproducible to within one millivolt can be secured by making the dilute solutions with water recently boiled and cooled in hydrogen, the dilution taking place in an atmosphere of hydrogen with the measurements being made while the hydrogen is bubbling thru the electrode vessel.
3. Using the precautions just described the electrode potential of zinc in 0.5, 0.1, 0.01, 0.002 N concentrations of zinc sulphate have been measured at room temperatures. Calculated values based on the electrolytic dissociation of zinc salt and these measurements are in good agreement with each other.

In a recently published article by Theodore Richards and Theodore Tunham Jr., they have shown the effect of changing hydrogen-ion concentration on the potential of the zinc electrode.

When a metal of weak basic character (such as gallium) is studied with regard to its zinc electrode potential, the salt solution in which the metal is immersed must be acidified to prevent hydrolysis. According-



In this paper I want to briefly indicate the results of a direct salt solution method of a typical type cell. I would like to illustrate experimentally the size and polarity of the potential difference thus caused.

Measurements of the potential of zinc in dilute solution of zinc sulphate measured against the calomel electrode (Hg +  $\text{Hg}_2\text{SO}_4$  sulphuric acid) can also directly against a zinc electrode containing zinc. The solution shows a rapid rise in potential as the acid concentration is increased.

The magnitude of this rise in potential indicates that it must be due to the liquid junction potential owing to the presence of the hydrogen ion.

Equal concentrations of  $\text{H}_2\text{SO}_4$  sulphate ion in the form of alkali sulphate added to the zinc sulphate solution gave small elevations in potential which were in the order of the transport number of the cations concerned. If it is assumed that the change in junction potential produced by sodium sulphate is small, one would find that about  $2/3$  of the change produced by the sulphuric acid is due to solution junction potential and the other third to a real increase in the single electrode potential of zinc, due to, presumably, a depression of the electrolytic dissociation of the zinc sulphate.

The results as obtained by these men are given in table 3.

In summing up the work of the aforementioned investigators, we arrive at the following conclusion: that there is direct bearing on the problem under consideration.

1. The size of the type of cell under consideration increases rapidly on standing. This may be prevented by using an acid electrolyte solution.



tion did not seem to be due to the presence of a zinc chloride solution.

2. Zinc chloride is soluble in water and gives a potential difference of 10 millivolt on the potential of the zinc metal.
3. Zinc electrodes in concentrated zinc chloride solutions potentials of zinc. Zinc with pure metal it is very difficult to prevent oxidation. If to exclude occluded gas a variable and unsatisfactory results are obtained.
4. Upon diluting zinc chloride solution hydrolysis takes place causing a change in concentration.
5. Zinc sulphate solutions give more constant results than those of zinc chloride.
6. For work with dilute solutions it is impossible to obtain reproducible results with a flowing electrolyte.
7. Electrode reproducibility within one millivolt can be obtained by mixing the "dry" solutions with water recently boiled and cooled in dry hydrogen, the dilution taking place in an atmosphere of hydrogen and the measurements made under this hydrogen atmosphere. Turn the electrode with 1.
8. Changes of several degrees in temperature have only a slight effect.
9. If the electrolyte is acid if it the potential is increased.
10. Last statement is to be in direct opposition to the results that were obtained by Forsell, for he stated before all his results were obtained by using a zinc chloride solution that was distinctly acid in character. This would tend to make his results higher than the theoretical values. It was due to this acid condition that it was all to prevent hydrolysis which otherwise would have led him into many difficulties.
11. It was with these conclusions that the organization of this problem was carried out.



22500.

$\text{ZnSO}_4 \cdot \text{H}_2\text{SO}_4$ .

N.	Total potential $\text{H}_2\text{O}_2$ in 1/20- normal dilution.	Effect of Potassium.	
		1. $\text{H}_2\text{O}_2$	1. $\text{H}_2\text{O}_2$ + 0.1% $\text{K}_2\text{SO}_4$
0.0	1.0777	0.0	0.0
0.1	1.0020	5.1	6.0
0.2	1.0571	19.4	21.0
1.0	1.1046	28.2	30.6
2.0	1.1172	59.2	45.3
4.0	1.1277	50.0	57.5
0.0 $\text{K}_2\text{SO}_4$	1.0771	( -0.6 )	0.0



### Experimental

In the following table are given the results of the zinc sulphate determinations. A standard cell was used as a standard cell, and a n/10 zinc sulphate solution as the reference electrode. An HCl solution was used as a buffer to eliminate liquid junction potentials.

The first series was run using an electrolytic zinc sulphate as an electrolyte. Very inconsistent results were obtained, the cause of which was later found to be partially due to the fact that the anodes were only partially saturated. In these determinations zinc sulphate solutions of 1, n/10, 1/100, 1/1000 concentrations were used. The results obtained in the n and n/10 concentrations were found to be fairly constant but were low due to the partial saturation of the zinc anodes. The results obtained in the 1/100 and 1/1000 solutions were ridiculously inconsistent, at times, the potential going in the wrong direction upon diluting the electrolyte.

It was thought advisable to try using zinc chloride instead of zinc sulphate as the contact solution. All attempts to dissolve chemically pure zinc chloride in water were unsuccessful due to the high degree of hydrolysis. The method used by Horsch was then resorted to, that is, dissolving pure zinc in a solution of hydrochloric acid of known strength. Platinum was used as a catalyst in aiding in the solution of the zinc, and the solution heated to boil in the reaction. After all reaction had in the zinc and hydrochloric acid had ceased the solution was tested with litmus and found to be distinctly acid. The excess zinc was then filtered off and this solution used as a stock solution. Upon diluting this solution to 1/10 hydrolysis took place, this necessitated refiltering the n/10 solution, consequently a lowering of the concentration. As the results desired were only to be approximate this fact was not taken into consideration.



Four amalgams were used containing 1, 2, 5, and 10% zinc respectively. The main intention in using these certain concentrations was to determine the point at which the amalgams would become saturated and whether or not that after reaching saturation the potential of the amalgams would remain constant with varying amounts of zinc, these amalgams being above the saturation point.

The amalgams were made by shaking chemically pure zinc in contact with mercury which had been purified with nitric acid and distilled.

The results obtained with the amalgams in contact with the 1 and 1/10 solutions of zincchloride showed a marked degree of consistency. They also showed that the electrode potential of the amalgam increases directly with the concentration of the zinc in the amalgam form up to the point of saturation. After the point of saturation has been reached the potential of the amalgam remains constant with an increasing concentration of the zinc. The results obtained for these two concentrations of electrolyte are given below.

Zn (amalgam)/ 1% ZnSO<sub>4</sub>/ 3 N KCl/ calomel.

% zinc in amal.	1.	2.	5.	10.
	e.m.f.	e.m.f.	e.m.f.	e.m.f.
-1.0925	-1.0990	-1.0990	-1.0917	
1.0927	1.0989	1.0985	1.0983	
1.0925	1.0990	1.0982	1.0985	
1.00925	1.0992	1.0987	1.0985	
1.0925	1.0982	1.0987	1.0985	
1.0925	1.0980	1.0987	1.0987	
1.0927	1.0979	1.0986	1.0986	
1.0927	1.0977	1.0987	1.0985	
1.0920	1.0977	1.0986	1.0985	
1.0922	<u>1.0975</u>	<u>1.0975</u>	<u>1.0975</u>	
ave. e.m.f.	<u>-1.0926</u>	<u>-1.0984</u>	<u>-1.0987</u>	<u>-1.0986</u>
E. P.	-0.7566	-0.7624	-0.7627	-0.7626



1. 1%  $\text{ZnCO}_3$ , 3%  $\text{KCl}$ , 1%  $\text{I}_2$ .

Zinc in amalgam	1.	2.	3.	10.	
c.m.f.	c.m.f.	c.m.f.	c.m.f.		
-1.1275	-1.1254	-1.1252	-1.1250		
-1.1272	-1.1255	-1.1250	-1.1252		
1.1271	1.1251	1.1250	1.1250		
1.1272	1.1247	1.1250	1.1251		
1.1270	1.1245	1.1250	1.1252		
1.1270	1.1240	1.1250	1.1252		
1.1268	1.1247	1.1250	1.1252		
1.1266	1.1244	1.1250	1.1250		
1.1265	1.1245	1.1250	1.1251		
1.1264	1.1245	1.1250	1.1252		
Ave. c.m.f.	-1.1270	-1.1248	-1.1251	-1.1251	
E. P.	-7910	-7980	-7991	-7991	

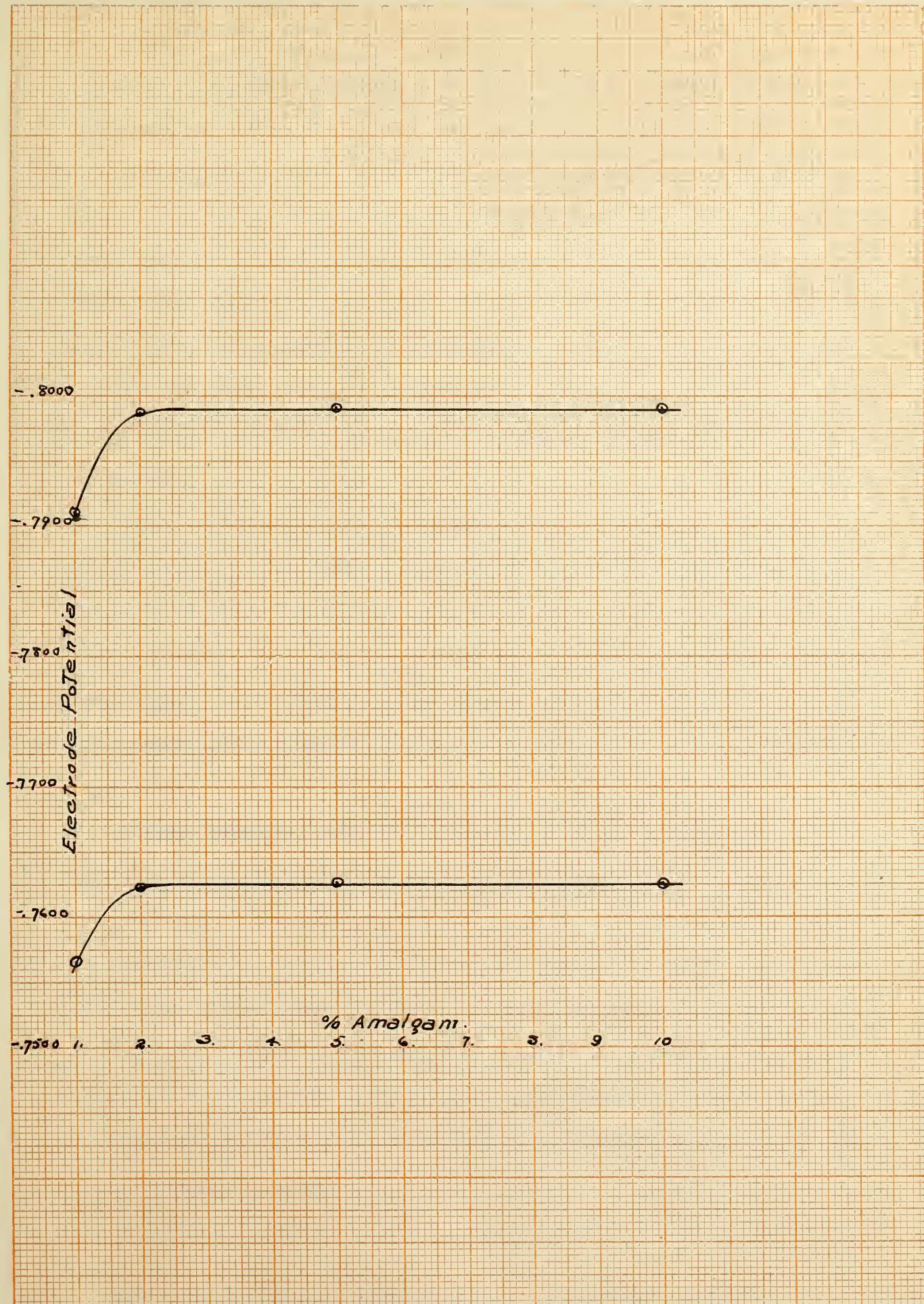
In plotting these results against the concentrations, it is shown that a zinc amalgam of between 2 and 5% zinc is saturated. It is also shown that after reaching the point of saturation the electrode potential of the metal remains constant.

The results shown here are by no means due to the inexactness of the concentrations of the solutions. But the relative values of the potential in 1% and 10% concentrations have very near the theoretical relation and show that in the more concentrated solutions of zinc chloride the potential of zinc can be determined with a fair degree of accuracy, and with a limited number of precautions.

These four amalgams were tried in the zinc chloride solutions of 1/100 and 1/1000 concentrations but it was impossible to obtain any constant or reproducible results. The method of using a flowing electrolyte was resorted to but seemed to have no effect on giving more constant values than those obtained with a stationary electrolyte.

In making these determinations an electrode vessel of the type shown in the illustration was used. In using a flowing electrolyte a funnel separating was inserted in the top of the vessel with the top of the funnel nearly touching the surface of the amalgam. The electrolyte was







run into the apparatus ~~and~~ and out to the side of the vessel, thus, at all times keeping the surface of the amalgam in contact with the electrolyte.

The amalgam was at all times kept covered with a concentrate solution of the zinc salt which kept it free from oxidation. Just before being used it was thoroughly washed with distilled water, and at all times kept out of contact with the air. In inserting the amalgam into the electrolyte vessel it was pipetted out of its container with a one c.c. pipette and run into the vessel already containing the electrolyte. These precautions were taken to prevent undue oxidation of the electrolyte and the amalgam by the air.

Since it was impossible to obtain results with saturated amalgam in dilute solutions, the finely divided metal was tried. This metal was obtained by electrolytic deposition from its salt solution and was obtained in its spongy form. As in the case of the saturated amalgam good results were obtained in the  $M/10$  zinc chloride solutions but in the more dilute solutions the same difficulties were encountered as in the previous experiments.

It was thought at this time advisable to check up the electrolytic zinc with the concentrated amalgam. As the results given in table 4. show, the potential of the spongy metal and the saturated amalgam agree within 0.4 millivolt this is close enough for the purpose for which this investigation was carried out. It shows that it is perfectly legitimate to use the saturated amalgam in place of the pure metal. In fact, it is highly advisable for it is much easier to get good contact and the readings are much more constant with the amalgam. It is easier to handle, and the surface strains are eliminated.



Electrolytic in  
zinc amalgam /  $1\text{M ZnCl}_2$  /  $3\text{M HCl}$  / 1 mol.

Electrolytic amalgm.	trit. amalgm.
e.m.f.	e.m.f.
-1.1153	-1.1156
1.1155	1.1154
1.1158	1.1153
1.1155	1.1153
1.1159	1.1153
1.1160	1.1153
1.1157	1.1154
1.1158	1.1152
1.1160	1.1153
<u>1.1159</u>	<u>1.1153</u>
Ave	<u>-1.1157</u>

Since it was impossible to obtain reproducible results of the potential of saturated amalgams in contact with the dilute zinc chloride solutions it was thought that this may have been due to the extensive hydrolysis of zinc chloride in solution. It was thought advisable to make one more attempt with zinc sulphate. As before very good results were obtained in the 1<sup>1</sup>/2 and 1<sup>1</sup>/10 concentrations but beyond this dilution the results were not constant, altho. much improvement could be seen over those obtained in the zinc chloride solutions.

In taking readings in the dilute solutions much difficulty was encountered due to their low conductivity. A means of remedying this trouble was tried and showed that the method had many possibilities. Since the trouble under consideration was due to the low conductivity of the solutions, the means of eliminating this consisted in adding some inert salt to the solution which would increase the conductivity and not effect the ionization of the zinc sulphate. .1 H was added to the 1M zinc sulphate to increase its conductivity. Four cells were tried containing 0.0, 5.0, 10.0, and 15.0 c.c. of .1 H HCl per 50 c.c. M zinc sulphate respectively. Checks on these cells were run and pure distilled water was used



in place of the HCl and to find whether or not the HCl had any effect on the potential. The results obtained are summarized.

In a 1. / .1 N HCl in 50 c.c. 11.1230, 11.1231, 11.1232.

.1 N HCl	0.c.c.	5 c.c.	10 c.c.	15 c.c.
	c.m.f.	c.m.f.	c.m.f.	c.m.f.
-1.1184	-1.1207	-1.1216	-1.1240	
1.1180	1.1200	1.1215	1.1232	
<u>1.1183</u>	<u>1.1205</u>	<u>1.1221</u>	<u>1.1235</u>	
Ave.	-1.1182	-1.1204	-1.1217	-1.1239
Diff. in m.m.	2.2	1.8	2.1	
Duplicate cell using water instead of .1 N HCl.				
1.1194	1.1215	1.1235		
1.1194	1.1214	1.1235		
<u>1.1194</u>	<u>1.1214</u>	<u>1.1231</u>		
Ave.	-1.1194	-1.1215	-1.1234	
Diff. in m.m.	2.1	1.9		

These results are hardly general enough to draw any conclusions from, but at least show that this procedure has possibilities. They also do not show us the effects in dilute solutions. The determination of these effects would constitute a problem in itself. But the limited amount of time no more work was done along this line except to make an attempt at using the HCl in the two dilute concentrations. It was found that more accurate readings could be obtained but as before the results varied.

In the first part of this article the results obtained by Moore and the conclusions arrived at by him were discussed. The method used by him was next tried. This method seems to have great possibilities and with the modifications given gave very satisfactory results.

The results in the dilute solutions were obtained by using a cell which heretofore had been used as a hydrogen electrode and seems to be the most satisfactory type that could be used with this method. The solutions were placed in this cell and thoroughly saturated with hydrogen before inserting the amalgam. The flow of hydrogen thro the electrolyte was con-



tinued during the entire process of insertion to solution and while the measurements were being made. One of the most striking effects of this method is that the surface of the amalgam remains bright four hours, while in the other methods tried the surface of the amalgam became coated with a grayish white precipitate after a very short time. From this effect it seems that the large deviation of results obtained in the dilute solutions, without being at all times saturated with hydrogen, was due to the hydrolysis of the electrolyte or the oxidation of the surface of the amalgam by the dilute electrolyte.

The results shown here for the potentials in the  $\text{M}$  and  $\text{M}/10$  solutions were obtained with ut the use of hydrogen since these results could be obtained with ut any difficulty and with an exactness which was sufficient for this purpose.

Those given for the  $\text{M}/100$  and  $\text{M}/1000$  solutions were obtained by bubbling hydrogen thru the electrolyte in the manner before described.

Zn amalgam / $\text{M ZnSO}_4$ / 3N $\text{KCl}$ / calomel.					
1.	time	2.	time	3.	time
-1.1280	1/45	-1.1277	1/45	-1.1269	1/51
1.1280	1/54	1.1272	1/55	1.1272	1/53
1.1276	1/57	1.1272	1/58	1.1271	1/59
1.1275	2/05	1.1265	2/08	1.1272	2/10
1.1270	2/11	1.1266	2/12	1.1272	2/16
<u>1.1270</u>	<u>2/17</u>	<u>1.1264</u>	<u>2/18</u>	<u>1.1269</u>	<u>2/20</u>
Ave.	<u>-1.1275</u>	<u>-1.1270</u>		<u>1.1271</u>	

Zn amalgam / $0.1\text{M ZnSO}_4$ / 3 N $\text{KCl}$ / calomel.					
-1.1505	9/45	-1.1497	9/56	-1.1494	9/54
<u>1.1507</u>	<u>10/00</u>	<u>1.1499</u>	<u>10/49</u>	<u>1.1497</u>	<u>10/52</u>
Ave.	<u>-1.1506</u>		<u>-1.1498</u>		<u>-1.1496</u>

Zn amalgam / $0.01\text{M ZnSO}_4$ / 3 N $\text{KCl}$ / calomel					
-1.1679	9/13	-1.1679	6/07	-1.1678	5/57
-1.1679	9/25	-1.1682	9/21	-1.1680	9/16
<u>1.1678</u>	<u>1/31</u>	<u>1.1679</u>	<u>1/28</u>	<u>1.1674</u>	<u>1/34</u>
Ave.	<u>-1.1679</u>		<u>-1.1680</u>		<u>-1.1677</u>



In sample // 0.001 M  $\text{ZnSO}_4$  / 3 M  $\text{HCl}$  / calomel.

1.	time	2.	time
-1.1923	1/46	-1.1919	1/45
1.1924	1/59	1.1922	1/50
1.1927	2/14	1.1927	2/12
1.1931	3/45	1.1935	3/43
1.1930	5/16	1.1935	4/26
<u>1.1930</u>	<u>5/41</u>	<u>1.1939</u>	<u>5/40</u>
Ave.	-1.1928		-1.1930

Average Results.

con.	e.m.f.	2. potential	Difference m.m.
electrolyte			
M.	-1.1272	-0.7912	
0.1 M.	-1.1500	-0.8140	23
0.01 M.	-1.1679	-0.8520	18
0.001 M.	-1.1929	-0.8570	25

If the results obtained are plotted with those obtained by Moore (as in the graph), it is seen that altho the results are not absolutely the same, due to only a necessary amount of precaution in the experimental work, they have nearly the same relation. This proves the unlimited possibilities of this method of determination and opens a large field of investigation.

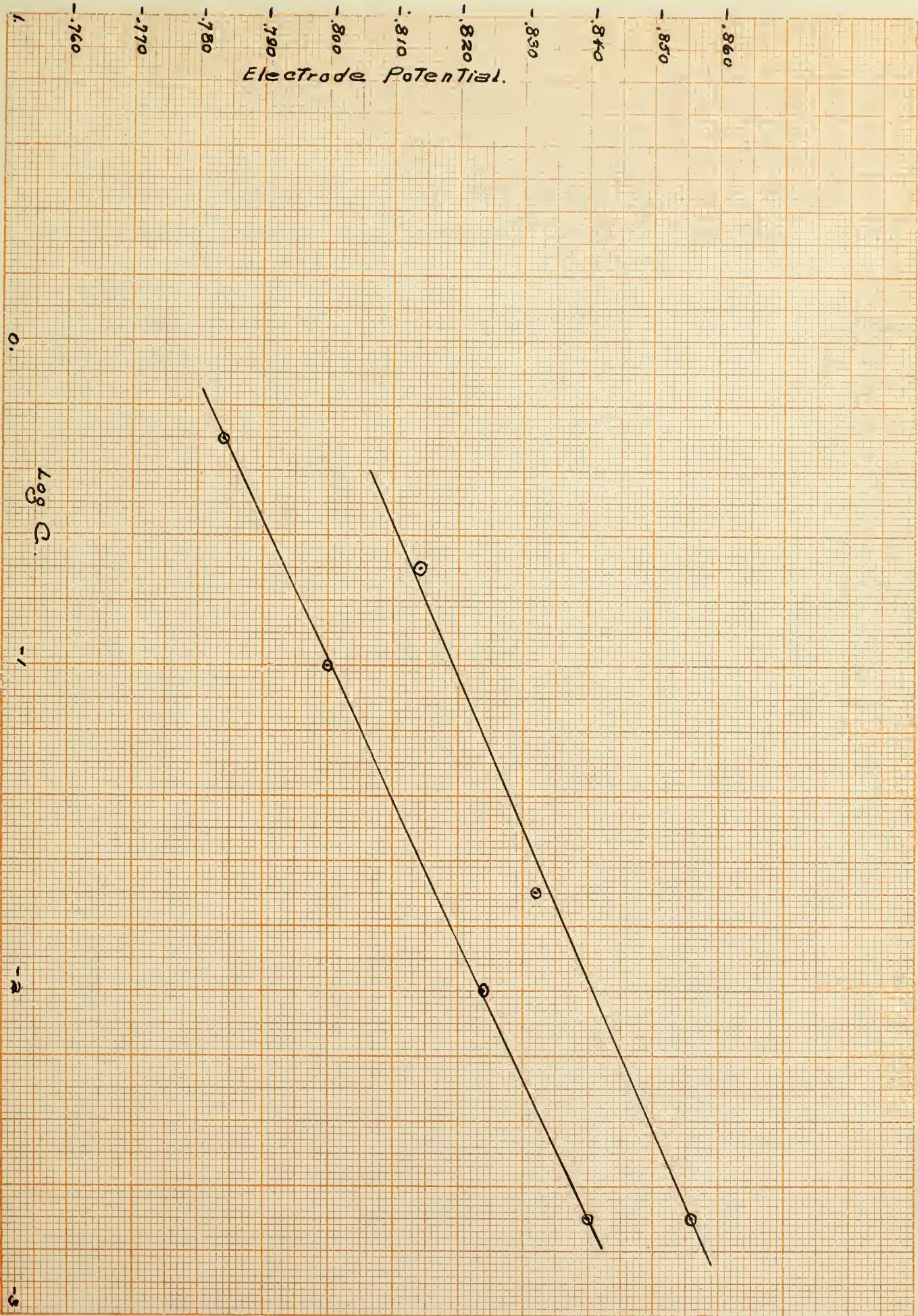


Conclusion and Summary.

1. It is difficult to obtain zinc chloride solution of constant concentration due to the high degree of hydrolysis.
2. The electrode potential of zinc amalgam increases directly with the concentration of the zinc in the amalgam form up to the point of saturation. After the point of saturation has been reached the potential of the amalgam remains constant with an increasing concentration of the zinc.
3. A saturated zinc amalgam contains between 2 and 3% zinc.
4. In the more concentrated solutions of zinc chloride the potential of zinc can be determined with a fair degree of accuracy and with a limited number of precautions.
5. It was impossible to obtain results with the saturated amalgam in dilute solutions even when resorting to a flowing electrolyte.
6. The potential of the spongy metal and the saturated amalgam agree within 0.4 millivolt.
7. The addition of HCl to the electrolyte to increase the conductivity was shown to have no effect on the potential in the concentrated solutions. Limited time prevented its trial in the dilute solutions.
8. Very good results were obtained in all dilutions by using a zinc sulphate solution saturated with hydrogen and bubbling a continuous stream of hydrogen thru the electrolyte while the readings are being taken.



Electrode Potential.





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